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Precision viscometry of extremely dilute solutions of high polymers

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PRECISION VISCOMETRY OF EXTREMELY DILUTE SOLUTIONS OF HIGH POLYMERS

INAUGURAL DISSERTATION

by

OLOV E. ÖHRN

FIL. LIC., VÄRML.

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With 17 figures in the text

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Preface

The present investigation was carried out at the Institute of Physical Chemistry of the University of Uppsala during the years 1954–1957.

I wish to express my deep gratitude to the Director of the Institute, Professor Stig Claesson, for suggesting this work to me and for his continuous interest, encouragement and helpful advice in frequent discussions and for his constant efforts to place the greatest possible facilities at my disposal.

I would also like to thank my colleagues and friends at the institute for good fellowship and stimulating discussions. Dr. Peter Dunlop has kindly revised the English text.

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Introduction

In recent years many attempts have been made in several laboratories to establish the viscometric behaviour of solutions of high polymers of different types at very low concentrations. It is of special interest to investigate if there is an observable change in this behaviour in the interval of the concentration, where the molecules lose direct contact with each other. This case has been studied theoretically; in particular by Simha (1) and Riseman and Ullman (2). Experimental studies have also been reported by Rothman, Simha and Weissberg (3), Takeda and Turuta (4), Streeter and Boyer (5), Umstätter (6), Kooy and Hermans (7), Tuijnman and Hermans (8) and others.

During 1950–1952 an apparatus for the accurate measurement of viscosity was designed and built at this Institute by Claesson and the present author (9). Here the experimental technique and some results of viscosity measurements of solutions of high polymers at extremely low concentrations are reported. During the course of this work it was sometimes desirable to modify the original design of the apparatus. Previously short reports on this research program have been published (10–12).

The work is presented in four parts. The first part briefly presents the theoretical and experimental background of the work. In the second part the viscometers used are described and the common errors of the viscometric measurements are discussed. The third part includes mainly the preparative work and the actual measurements of the viscosity. Finally in the fourth part the results of the measurements are presented and discussed.

Uppsala, March 1958

PART I

THEORETICAL AND EXPERIMENTAL BACKGROUND FOR THE PRESENT WORK

Chapter 1. Some theoretical aspects concerning viscosity at wery low concentrations and the conception of "critical concentration"

Simha (1) and Riseman and Ullman (2) have discussed theoretically the dependence on concentration of viscosity in dilute solutions. The result obtained indicates, that in dilute solutions of chain molecules the numerical value of k' in Huggins' equation

$$\eta_{sp}/c = [\eta] + k'[\eta]^2 c \qquad (1)$$

ought to be of magnitude 0.6–0.8 instead of 0.3–0.4 as is usually found experimentally. It is possible that these lower values are due to the fact that in general the measurements can only be made at such high concentrations that the assumptions given at the theoretical discussion are not valid.

Various attempts have been made to calculate the "critical concentrations", at which the polymer molecules lose direct contact with each other. Boyer and Spencer (13) have proposed the following definition of the "critical concentration". "The critical concentration" is the concentration corresponding to the hexagonal close-packing of spheres with diameters two times those obtained for the random coils of the molecules in question in the actual solvent. The factor *two* is introduced arbitrarily. This definition means that for polystyrene with $M = 10^6$ the "critical concentration" in benzene would be 0.0003 g/ml. But the hydrodynamically effective sphere is greater than the geometric volume the molecule occupies. Thus it may be supposed that the effects of the "critical concentrations" will take place at lower concentrations if hydrodynamic methods of measurements are used. Doty and Steiner (14) and others also found that for measurements with static methods the "critical concentrations" ought to be surprisingly high. (Many of these questions are discussed by Frisch and Simha in the monograph on Rheology, edited by Eirich (15).)

As to which solution of polymer is most suitable for an examination of these facts, the following may be said. The "critical concentration" increases with decreasing molecular weight, but as the specific viscosity probably decreases at the same rate it appears as though the specific viscosity, at which the "critical concentration" effects may be observed, is rather independent of molecular weight. In the same manner it may be independent of the type of solvent, good or poor. But there are yet some factors to be considered. Measurements with solutes of relatively low molecular weight are often easier to perform. On the other hand it is possible that in the change from a purely hydrodynamic interaction between the molecules to an interaction due

to direct contact when the "critical concentration" is passed, the change of energy dissipation is greater for larger molecules than for smaller ones. Thus the larger molecules will give a greater change in the viscosity curve at this concentration. It is also possible that this effect will be even greater for solutions in poor solvents since, in this case, the molecules are more compact and stiff.

Chapter 2. Earlier results of measurements of viscosities at very low concentrations

Some time ago it was reported (16, 17), that sometimes in a diagram of η_{sp}/c vs. c a linear relationship was obtained down to a rather low concentration, but at still lower concentrations there was a "bending down" of the curve. During recent years however the results obtained with apparatus especially designed for the investigations of this phenomenon have been particularly divergent. Rothman, Simha and Weissberg (3) found for polystyrene in toluene a linear relationship down to the lowest concentrations at which measurements could be made. Takeda and Turuta (4) found that the curve in question "bent upwards". They worked with polyvinyl chloride in cyclohexanone. Approximately the same result was obtained by Streeter and Boyer (5) with polystyrene in toluene and methyl ethyl ketone. This effect was assumed by Streeter and Boyer to be due to the entangling of the polymer molecules at these low concentrations. They also concluded that Rothman, Simha and Weissberg, using a viscometer of the dilution type, did not find this "bending up effect" because there was not time enough after the dilution in the viscometer for the molecules to disentangle and expand to a new position of equilibrium. But Streeter and Boyer also found that the curve after "bending up" reached a maximum and then tended to go down very abrubtly at still lower concentrations. This was explained as an adsorption effect similar to that described by Cutler and Kimball (18); the concentration was diminished in the viscometer due to the adsorption of polymer molecules on the walls of the viscometer. Results similar to those of Takeda and Turuta and Streeter and Boyer were also obtained by Umstätter (6) with measurements on polyisobutylene (Oppanol) in decalin. Batzer (19) found that branched polyesters in different solvents gave a minimum–maximum curve in contrast to linear polyesters with which he obtained a linear relationship down to a relatively low concentration, and then there was a "bending down". He also found the same type of curves for polyvinyl chloride, branched and linear, in tetrahydrofuran. Menčík and Láníková (20), on the other hand, did not succeed in proving such a difference in the viscometric behaviour of solutions of branched and linear molecules, respectively. They also used polyvinyl chloride in cyclohexanone and tetrahydrofuran. In two of the preliminary reports by the present author (11, 12) these anomalous viscosity effects were discussed in terms of the thickness of the adsorbed macromolecular layer and reduction of capillary diameter. Kooy and Hermans (7), with an apparatus with the highest precision previously used, got a linear relationship for polystyrene in toluene down to the lowest concentrations. Tuijnman and Hermans (8), with the same apparatus as Kooy and Hermans but with some improvements, worked with polyvinyl acetate in toluene. They concluded that "in the system PVA-toluene the anomalous viscosity-concentration curve is due primarily to non-Newtonian effects".

Some of the works here mentioned will be commented on later in connection with the results now obtained (pp. 424, 432).

PART II

VISCOMETERS AND ERRORS OF VISCOMETRIC MEASUREMENTS

Chapter 3. Construction of the precision viscometers used

A. *General considerations*

From the previous measurements of the viscosity of high polymer solutions there is no doubt that, if there shall be any chance at all to solve the actual problem of viscosity, one must be able to measure a specific viscosity as low as 0.01 with an accuracy of at least one per cent. This also means that the viscometer totally must have an accuracy of at least 1 part in 10,000. But as the final error in the measurement is composed of errors from different sources, it is probable, that one ought to demand that the accuracy at each individual source of error be at least 1 part in 100,000.

B. *A general survey of the viscometers used*

During the construction of the viscometer it was also obvious, that it was only by using a capillary viscometer that the desired accuracy of 1 part in 100,000 could be obtained in each individual source of error. First of all an Ostwald viscometer was constructed. This construction was essentially based on the results published by Jones *et al.* (21–23) from some precision viscometers constructed in the 1930's. The real viscometer had the following dimensions and constants:

Efflux volume, 20 ml	Capillary diameter, 0.44 mm
Mean hydrostatic head, ~20 cm	Efflux time for water (25°C), ~1100 s
Capillary length, 24 cm	

Later an Ubbelohde viscometer was also constructed. It had about the same dimensions as the Ostwald viscometer.

In the recent years the apparatus has been rebuilt thoroughly, and two new viscometers have been constructed. The principal difference between these viscometers and the older ones is, that now the liquid in the viscometer is not pressed into the upper viscometer bulb as earlier, but comes to that bulb, when we tilt the whole viscometer. In that way we can have the viscometer totally closed when working with it, which can be of great importance: no evaporation and avoidance of dust.

Fig. 1 shows the apparatus in the present state.

A total view of the apparatus before the last great rebuilding may be seen in a paper by Claesson (9).

C. *The construction in detail*

In the description of the apparatus we have discussed, in part, some of the errors which may occur in the viscosity measurements and in this way some of the principles used in the construction of the viscometers become evident. It is also necessary to discuss some of the details of the apparatus in the next chapter, which deals with experimental errors.

1. *The Ostwald viscometer*

The modified Ostwald viscometer now used is shown in Fig. 2. The liquid is brought to the upper bulb *A* by tilting the whole viscometer (in the direction of the arrow).

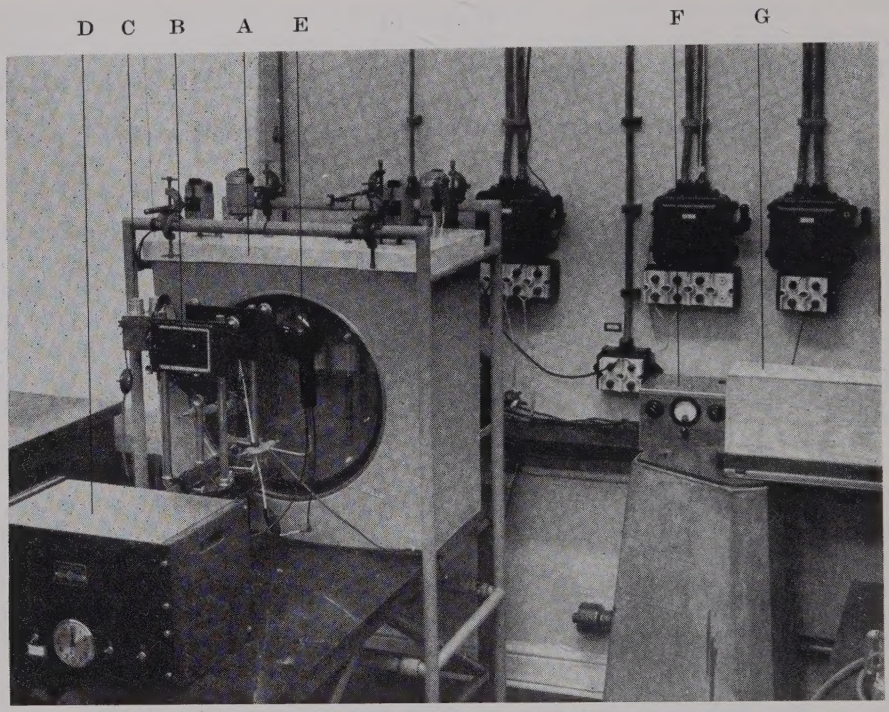

Fig. 1. High precision viscometer. *A*, thermostat; *B*, camera; *C*, clock; *D*, vacuum precision fork; *E*, electronic flash lightening tube; *F*, electronic control unit; *G*, casing for galvanometer and photo tube arrangement.

In doing so the liquid will first be emptied from the lower bulb *B* to a reservoir *C*, and then with further tilting it runs into *A*. The liquid left in the capillary from the preceding run will now be forced up into *B*. The viscometer is held in this inverted position for some time after *A* and the whole capillary are filled, so that as much as possible of the liquid remaining on the walls of *B* will run out of B. It is not tilted back until it has been in that inverted position long enough so that the variations of the mass of the liquid in the remaining liquid film do not influence the volume in *B* too much in the following measurement. If this is not the case the height of the liquid in *B* is changed so that the maximum error allowed in the hydrostatic head will be exceeded. The "last" drop of the liquid will be hanging on the tongue *D* and will fall into *C*, when the viscometer is tilted back again. Here it is essential that the connection between the capillary and *B* is made in such a manner, that the part of the liquid film that tends to flow towards the capillary will not be so large, that one runs the risk of getting air bubbles enclosed in that position. When tilting the viscometer back it is first placed in a horizontal position (Fig. 2*b*). Then some of the liquid will be kept separate and stays between an arbitrary point on the lower part of the capillary *E* and the tip of the little bulb *F*, whereas the rest of the liquid runs into *C*. Afterwards the viscometer is turned carefully, so that a little of the liquid cut off flows away at *F*. This ensures, that the other meniscus comes to a fixed mark about

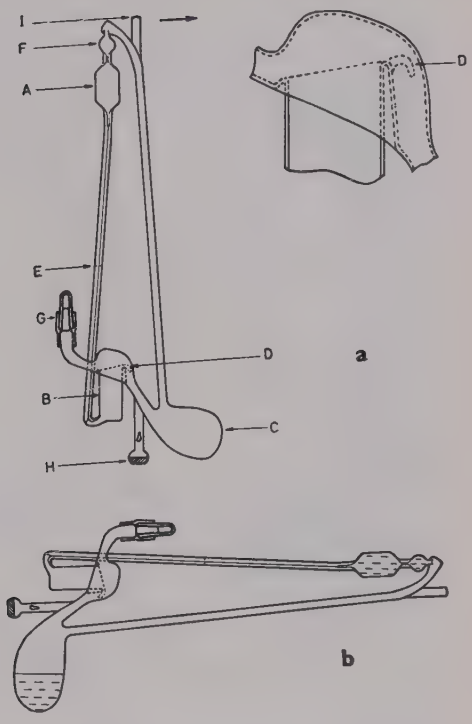

Fig. 2. Ostwald viscometer. (*a*) In position for measurement. (*b*) In position for adjusting of working volume.

the middle of the capillary *E*. This volume separated from the rest of the liquid will be used in the actual measurement of the viscosity. Then the connection between the capillary and the bulb *B* has such a shape that, when finally the viscometer is turned to the position for measurement, the irregular lowest part of *B* is completely filled with liquid when the bulb *F* is empty.

2. *The suspended level viscometer*

The suspended level viscometer is shown in Fig. 3. This viscometer has been constructed to permit simultaneous measurements to be made in three capillaries with different diameters. The reason for this arrangement will be given in the next chapter (see p. 413). There it is also pointed out that it is desirable to get about the same velocity gradient in all the capillaries. This has been obtained by holding the mean hydrostatic head about the same in all cases, whereas the wider capillaries have been made longer so as to give approximately the same maximum velocity gradient. To get similar efflux times for all the three capillaries, the upper bulbs have also been constructed with different sizes. The three different viscometers, which really constitute this suspended level instrument are in the following designated S1, S2 and S3, S1 having the widest capillary.

3. *Some details common for both viscometers*

The capillary of the Ostwald viscometer has the same diameter and length as that of S1 in order to get easily a comparison of the two types of viscometers. The corre-

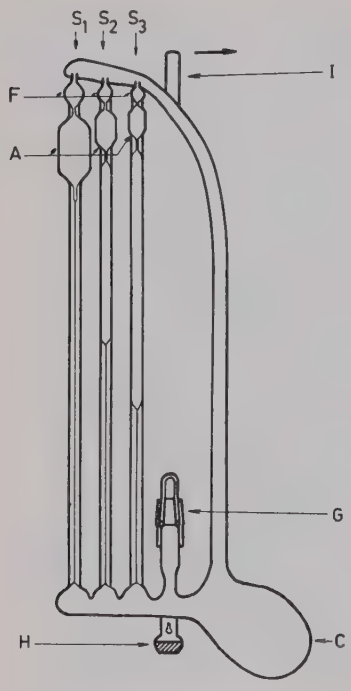

Fig. 3. Suspended level viscometer with three different capillaries.

sponding bulbs are also of about the same sizes. All capillaries are precision bored (Veridia). The ground glass joint *G* is made tight with a polytetrafluoroethylene sleeve (Longhborough Glass Co.) and is shown in the figures with a rubber tube outside the cap (see also p. 419).

The viscometer is fixed in the holder in the thermostat by pressing the ball ground joint *H* by means of a spring (not shown in the figure) against a conical hole, while the tap *I* at the top of the viscometer is pressed against a V-shaped track in the holder by a piece of metal covered by a rubber sheet. Then to get the viscometer in its right position it is turned round its vertical axle so that the "backside" of the reservoir *C* is pressed against a metal head on the holder. In Table 1 some of the most important dimensions and constants of the viscometers are given.

4. *The thermostat*

When the temperature is changed, the viscosity of the liquids used as solvents for viscosity measurements of the type here described is changed about 1–2 per cent

Table 1. Viscometer dimensions and constants.

Viscometer	Ostwald	S1	S2	S3
Efflux volume, ml	25	25	10	3
Capillary length, cm	40	40	24	17
Capillary diameter, mm	0.5	0.5	0.3	0.2
Flow time for water at 25°C, s	1460	1350	2340	1700

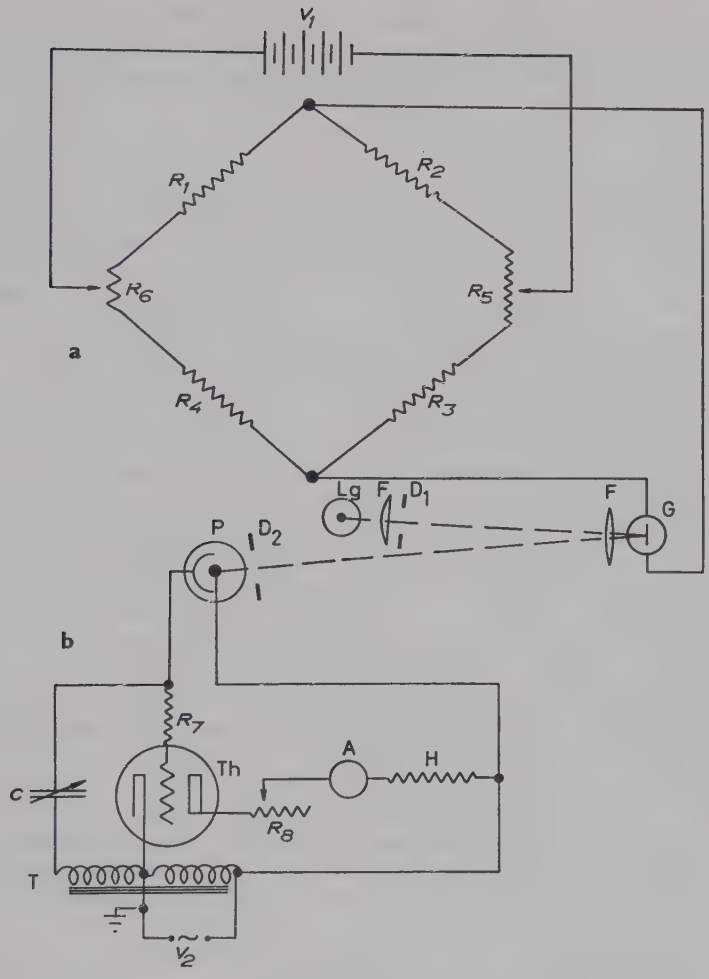

Fig. 4. Wiring diagram for temperature control unit. (*a*) Wheatstone bridge. (*b*) Electronic control unit.

per degree (C). (The change of the efflux time of a viscometer is about the same for a given liquid.) Thus to get a relative error of only 1/100,000 a constancy of the temperature of better than 1/1000 of a degree is required. Therefore we have done a great deal of work with the thermostat.

The thermostat vessel is made of aluminum, 70 × 70 × 30 cm, and insulated with 5 cm of soft foam plastics. The cover is insulated with 5 cm of stiff foam polystyrene. In the front of the thermostat there is a round glass window (diameter 50 cm) insulated with two sheets of acrylate glass, placed so that two air layers (1 cm thick) are obtained, thus increasing the insulation effect.

For heating there are two heaters using constant current but also two more taking

current, which is regulated by a resistance thermometer. These last heaters normally generate only a few watts. If the temperature for some reason sinks more than about one hundredth of a degree from the desired temperature, a common contact thermometer activates a further heater. This precaution ensures, that abnormally high currents through the galvanometer included in the resistance thermometer wirings shall be avoided.

The principle that is used for the regulation of the heater current by the resistance thermometer, has been recommended for instance by Müller *et al.* (24). In Fig. 4 a wiring diagram is shown. The organ that is sensitive to the temperature in the thermostat is the nickel resistances R_1 and R_3 in the two opposite arms of a Wheatstone bridge; the other two resistances R_2 and R_4, made from manganin are rather insensitive to temperature. At the right temperature the bridge is adjusted so that no current will flow through the null instrument, G, a mirror galvanometer. Then the light that is thrown by the galvanometer mirror in the direction of the photo tube P will fall only partly on P and diminish its resistance. The boundary of the area of the light falling on P is well defined by means of two diaphragms D_1, D_2. Thus the thyratron Th is fired for part of every period so that the current through Th and thus also through the heater H will precisely compensate the heat loss of the thermostat. If the temperature, for some reason or other, sinks a little, the resistances R_1 and R_3 diminish, and the bridge is no longer balanced. Thus the galvanometer deviates so that a little more of the light from its mirror falls on the photo tube. Then the thyratron fires earlier during the period, and more current will go through the heaters. This gives of course a proportional control of the temperature.

The electrical insulation on the nickel resistances should permit good thermal contact with the thermostat water and yet be completely watertight. This has been provided by constructing the resistances in the following way. On a thin-walled tube of brass (length 45 cm, diameter 18 mm) treated with a silicon lacquer the resistance wire was bifilarly wound, and then it was lacquered. Outside this unit another tube of brass, as narrow as possible, was placed and soldered to the first one at the lower edge. To raise the temperature sensitivity of the whole equipment further, the water of the thermostat is pumped through the inner tubes by means of centrifugal pumps applied at the lower ends of two of the four stirrers totally used. With the present construction of the resistances a difference in temperature between the resistance wire and the water of the thermostat will be diminished by half in a time shorter than a second. By having the area of the resistances and the length of the wires relatively great it is also sure that the temperature of the resistances will be only very little higher than that of the water, in spite of the heat which must be produced in the bridge.

Perhaps it should be pointed out that not only the nickel resistances but also the rest of the Wheatstone bridge are placed in the thermostat, as this is of course the simplest way to keep it as electrically constant as possible.

The coupling elements and other details included in the Wheatstone bridge and in the electronic control unit are listed below.

The Wheatstone bridge

R_1, R_3 1000 Ω nickel	R_6 5 Ω Helipot potentiometer
R_2, R_4 1000 Ω manganin	G galvanometer
R_5 100 Ω Helipot potentiometer	V_1 10 V lead storage battery

The wire of R_1 and R_3 is made from a very pure nickel quality (British Driver-Harris Co. Ltd), diameter 0.06 mm.

The electronic control unit

Th	Raytheon 2050. Two units in a parallel coupling	*H*	heater
P	RCA 1 P 37	*T*	auto transformer
C	0–50 pF	V_2	127 V ~ stabilized
R_7	1 MΩ	*Lg*	galvanometer lamp (white light)
R_8	0–1000 Ω	*F*	lenses
A	0–1 A amperemeter	D_1, D_2	diaphragms

As heaters two rod-shaped incandescent lamps (Skandia 4 B, 40 W, 220 V) are used, each connected in series with one of the thyratrons. As their heat capacity is very low, they react rapidly, if the current through them varies.

For control of the temperature a Beckmann thermometer is used. But it is also possible to control this by observation of the position of the light spot on the photo tube. Fluctuations of the temperature of very short duration are easy to follow, due to the fact that the nickel resistances change their values very quickly.

With such a proportional control of the temperature it is impossible, as was pointed out by Claesson (26), to be quite independent of the temperature of the room. A fall in the temperature of the room will immediately result in a drop of the equilibrium temperature of the thermostat. The sensitivity of the equilibrium temperature to the variations in the room temperature is of course for a given thermostat wholly dependent on the capacity of the thyratron to compensate a sinking of the temperature and thus on the maximum power obtainable from the same. In this actual case it is enough to hold the variations of the temperature of the room within six tenths of a centigrade degree by means of a simple arrangement for thermostating. The constancy of the position of the equilibrium temperature is of course in the same way dependent on the variations of the energy that is brought to the thermostat in other ways than by the control unit. Most important of these effects is the heat added by the constant heaters and the stirrers, and for this reason only stabilized current is used in the whole equipment.

5. *The measurement of the efflux time*

A photographic method is used for the measurement of the efflux time. A photograph is taken of the timing marks, above and below the upper viscometer bulb, and also on the same plate a running clock (via a mirror), just as the meniscus passes these marks. By means of a comparator the distance between the meniscus and the actual mark is measured. Then it is easy to correct the time given by the clock on the photographic plate to the time when the meniscus really passed the mark, if only the velocity of the meniscus is known. This velocity is obtained from a photograph with two exposures of the meniscus on the same plate taken in the course of a few tenth's of a second. In that way the efflux time will be determined in an objective manner with an accuracy that practically is limited only by the accuracy of the clock used.

In these measurements we use a Jaquet clock with synchronous motor works. It receives its alternating current from an oscillator, a Type 816 vacuum tube precision fork, General Radio Co., in which the thermostated fork presses its own frequency on the output voltage. The output power is two watts maximum and this is quite enough for the clock without any amplification.

The camera, designed with magazine for plates, 9 × 12 cm, is mounted on a heavy optical bench. A Zeiss Tessar Objective, 1:6.3, f = 10.5 cm, is used. At a distance of 25 cm an image of the viscometer and the clock, with a reduction of 0.7, will be obtained. The photographic plate is Gevaert Gevachrome, 32°. In the actual photographing some different procedures are applied. Recently the light source has been a synchronized electronic flash lightening tube, Braun Hobby Standard with a power of 60 watt-seconds. The two exposures for the determination of the velocity of the meniscus are obtained by means of a special shutter in which a plate of metal with two slits slides past the objective lens with a suitable velocity at the same time as the viscometer and the clock are illuminated, each with a photographic lamp of 150 watts.

Chapter 4. Sources of errors. Accuracy and corrections of the viscometers used

A. *General considerations and a list of the errors discussed*

In the discussion of the errors of the viscosity measurements some of the most well-known errors in such measurements will be treated, but in addition some other errors will be discussed. These later are of two different kinds: errors of general importance for viscosity measurements and errors dependent on the special type of viscometers used here.

The viscosity measurements of the kind reported here are of course based on the modified Poiseuille's law

$$\eta = \frac{\pi r^4 h \varrho g t}{8 V l} - \frac{m \varrho V}{8 \pi t l}, \tag{1}$$

where η is viscosity, r radius, h hydrostatic head, ϱ liquid density, g acceleration due to gravity, t efflux time, V efflux volume, l capillary length, and m a correction constant. When the errors are described here, it has been considered more suitable not to discuss the individual factors in this equation separately. Sometimes a special source of error has been observed and then its influence on the different factors in Poiseuille's law is discussed. It is perhaps suitable to point out here again that we have endeavoured to insure that all individual, relative errors do not amount to more than 1/100,000.

The following errors will be discussed:

1. Temperature
2. Time measurements
3. Drainage
4. Inclination of the viscometer
5. Surface tension
6. Working volume (Ostwald viscometer)
7. "Kinetic energy"
8. Barometric pressure
9. Adsorption

This classification of errors is not rigorous. Small errors in connection with the errors in one of the above groups are sometimes treated here, even though they do not belong to the group in question. Some accidental errors are very difficult to estimate theoretically. They will only be discussed in part 3 in connection with cleaning and preparations.

From the detailed discussion below it is obvious that it has been considered suitable to design the apparatus so as to reduce the errors Nos. 1–6 to within the permitted limits, whereas for the errors Nos. 7–9 corrections are usually applied.

B. *Discussion in detail*

1. *Temperature*

As already stated an accuracy in the temperature of better than 1/1000°C is sometimes needed (the viscosity is changed by 1 to 2 per cent per degree and the density by 0.1 per cent). For this reason the resistance thermometer of the thermostat (p. 406) has been constructed so that a change in the temperature of 1/1000°C will give a deviation of the galvanometer great enough to cause a change in the position of the light spot on the photo tube by about 3 mm (at a distance of 0.6 m). Then as the drifting of the zero position of the galvanometer usually does not amount to more than 1 mm during relatively long periods, there is no difficulty in maintaining the temperature with the required accuracy. In general the error seems to be not greater than 1/2000°C.

Besides the error in the temperature which depends on the thermostat there is another caused by the heat of friction in the viscometer. This occurs partly when the upper bulb is filled and partly in the capillary during the measurement. But after the filling of the upper bulb the viscometer is held in the inverted position for so long time, that the liquid surely adopts anew the temperature of the thermostat. Then during the measurement there is, with water as solvent, a difference in temperature of 1/1000° between the two ends of the capillary, if we assume the process to be adiabatic (the corresponding difference for organic solvents is twice this value). But since we calculate that a certain amount of heat is lost through the capillary and since the variations in this temperature difference are small compared to the difference itself, this effect is negligible. It also seems possible to compare directly the results from the capillaries with different diameters in spite of different temperature increments.

Finally it may perhaps be said that the influence of the temperature on the dimensions of the viscometer is of little importance in this connection.

2. *Time measurements*

The vacuum tube precision fork used in the equipment for the measurements of the efflux time has a stability of the frequency guaranteed to be at least 1 part in 100,000. This has been checked over long intervals against the standard time signal. The fastest hand of the synchronous clock, which makes one turn per second, has also been checked to see if its speed is the same during the whole turn. This has been done by taking photographs of the running clock with the fastest hand in ten different positions and on the same plates a scaler. These checks demonstrated that the clock had the accuracy required.

The efflux times for the solvents used have not usually been much shorter than 1000 seconds. In this case the accuracy required is 1/100 of a second. On the photographic plates (p. 407) it is easy to decide the position of the fastest hand with better accuracy than 1/100 of a second. When the Ostwald viscometer and the S1 viscometer are used, the velocity of the meniscus, when passing the timing marks, is such that 1 mm on the plate corresponds to a time of 3–6 hundredths of a second. For the S3 viscometer however the velocity of the meniscus is only about a tenth of that for S1, and to get the same accuracy again in the correction it is necessary to measure the actual distance within some hundredths of a mm; this is usually quite easily done with the comparator. (A reduction of the diameter of the capillaries above and below

the upper viscometer bulb to get higher velocities has not been considered as advantageous. A production of small drops would easily take place in the upper capillary.)

3. *Drainage*

According to Jones and Stauffer (22) the drainage in a capillary viscometer is approximately independent of the kinematic viscosity if the liquid flows only under the influence of its own weight. Of course it is claimed that the measurements are always made in the same manner. Thus it is necessary, for instance, that the liquid is raised to the same height above the upper viscometer bulb, so that the drainage always will come from the same surface. This will be done automatically in the viscometers used here, as the additional little bulb *F* (Figs. 2 and 3, pp. 403 and 404) is always filled before the measurement and it is impossible for the drainage from outside to enter it.

The drainage in the lower bulb of the Ostwald viscometer must also be observed. This will of course not change the efflux volume but only the hydrostatic head. In this case it is made as small and as reproducible as possible by holding the viscometer in the inverted position a relatively long and definite time (15 min). From tests it seems as if the total drainage for the lower bulb does not reach the maximum error of the volume that is allowed.

4. *Inclination of the viscometer*

As the Ostwald viscometer is of the oblique type with the two viscometer bulbs directly above each other, and as the mean hydrostatic head is approximately the same in all cases for both viscometers, we almost always must have the same error due to the inclination of the viscometer. Thus with a hydrostatic head of 40 cm and with, for instance, the lower meniscus fixed, the maximum variation in the upper bulb should not be greater than 3 mm in any direction. But actually the maximum displacement allowed is surely determined by the error in aligning the upper bulb above the lower during the construction of the viscometer. An error of about 5 mm in this alignment would diminish the maximum displacement described above to only $\frac{1}{3}$ mm. Such errors have not been exceeded in this work.

5. *Surface tension*

The errors dependent on surface tension are among the most difficult to overcome. To eliminate the effect completely for troublesome systems (water solutions of surface active substances for instance) by constructing the apparatus in a suitable manner seems to be practically impossible. Different methods to correct for the effect have been worked out both on theoretical and experimental bases, but usually they are most difficult to use (23, 25). In this work however the Ostwald and the suspended level (S1) viscometers must have different signs for the error obtained due to the dimensions of the different menisci, and then it is of course relatively easy to decide if corrections are necessary. For the organic solvents used they seem to be negligible.

6. *Working volume (Ostwald viscometer)*

With the construction used here where the working volume intended for a measurement is determined anew for every individual flow and is only a part of the liquid existing in the viscometer, the volume of this liquid may of course be varied within very wide limits. The maximum error allowed in the actual working volume may be

2 mm³. This error is determined by the position of the meniscus at the mark on the capillary E (see Fig. 2*a*, p. 403) and at the tip of F. An error as great as 0.5 mm at E, and which is surely never exceeded, gives an error in the volume of only 0.1 mm³. The error at F could easily be greater but it never seems to amount to as much as 1 mm³. During tests it has been possible to make the total error smaller than 0.2 mm³.

7. *"Kinetic energy"*

The "kinetic energy" correction of the specific viscosity η_{sp} is determined approximately for diluted solutions by the following formula derived by Schulz (27):

$$\eta_{sp} = \{\eta_{sp}\} (1 + 2 B/t_0^2). \tag{2}$$

Here $\{\eta_{sp}\}$ is the uncorrected value of the specific viscosity and B is a constant characteristic of the apparatus (see below). Thus when the kinetic energy correction is applied to the primary values of the specific viscosity, a plot of η_{sp}/c versus c will be a curve parallel to but displaced upwards from the curve obtained when the uncorrected values were used. In an investigation such as this, which primarily deals with the shape of the curve and not the value of $[\eta]$, the error due to the "kinetic energy" has, contrary to what has been occasionally asserted, a diminutive importance by itself. On the other hand, due to the importance of the position of the experimental curve when we want to discuss the adsorption of polymer on the walls of the capillary, it is very important to be able to determine the "kinetic energy" correction with great accuracy. This adsorption will, in certain cases, have a great influence on the shape of the curve.

None of the methods for the determination of the "kinetic energy" correction usually recommended in the hand books of viscosity has been considered as adequate in its original form. But by modifying one of these methods in a suitable manner a satisfactory result has been obtained.

Poiseuille's law corrected for the "kinetic energy" error (Eq. (1)) may be written as

$$\eta = \varrho A (t - B/t) \tag{3}$$

where A and B are constants of the apparatus, and the term $\varrho A (B/t)$ is the "kinetic energy" correction. If the values of A and B are known, it is possible to calculate the viscosity of a liquid from its flow time. To measure A and B it is usual to determine the efflux times for two liquids with known viscosity and density, and then to calculate A and B from Eq. (3). When evaluating the constants we get (indices 1 and 2 refer to liquid 1 and 2 respectively, $\nu = \eta/\varrho$ is the kinematic viscosity):

$$A = \frac{\nu_2 t_2 - \nu_1 t_1}{t_2^2 - t_1^2}, \tag{4}$$

$$B = t_1 t_2 \frac{\nu_2 t_1 - \nu_1 t_2}{\nu_2 t_2 - \nu_1 t_1}. \tag{5}$$

But the primary aim of this work is to determine relative viscosities and not absolute ones and hence it is not necessary to know the value of A but only that of B. From Eq. (5), which may be written as

$$B = t_1 t_2 \frac{t_1 - t_2 (\nu_1/\nu_2)}{t_2 - t_1 (\nu_1/\nu_2)}, \tag{6}$$

it is possible to calculate B from the flow times of two liquids if we only know the quotient between their kinematic viscosities. But for a capillary viscometer, where the "kinetic energy" correction may be neglected:

$$\nu = \text{constant} \times t, \tag{7}$$

and thus it is possible to determine the quotient between the kinematic viscosities of two liquids by measuring the flow times in such a "correction free" viscometer. There is no great difficulty in constructing capillary viscometers with arbitrarily small "kinetic energy" corrections, *if they are only designed to be used for occasional measurements with low molecular liquids.* Such viscometers will necessarily have very long efflux times. This fact among others causes that they are not convenient for common use.

In connection with some measurements to estimate the influence of shear rate on the viscosity results obtained, a new viscometer was recently constructed (see p. 426). This is of the Ubbelohde type, and as it gives very low "kinetic energy" errors and is rather easy to work with, the last determinations of B have been made by means of this. Its dimensions and constants are: Capillary lengths 150 cm, radius 0.15 mm, driving head ~ 30 cm, relative error due to "kinetic energy" $\sim 1/100{,}000$ for water.

Among the advantages of this modified method the following will be mentioned. If the values of the viscosity and density of a liquid are taken from works of reference, it is necessary to be certain that the preparation of the liquid used for the calibration is exactly the same as that used by the observer in the reference. With this new method on the other hand, the calibration liquids need only be free of dust. Thus we are free to choose reference liquids as we please, and it is possible for instance to choose a mixture of two liquids or more. In practice the dimensions and properties of a viscometer will vary a little with for instance different surface tensions (and thus A and B are not real apparatus constants, if we do not take the surface tensions into consideration). It may then be convenient in the determination of B to use partly the solvent to be used later and partly one or still better some liquids with other viscosity values. But it is very convenient if not only the surface tension of these liquids but also other physical properties, which may influence the efflux time, are as similar to those of the solvent as possible. Then for measurements on macromolecular solutions it may be of importance that the quotient of the efflux times, from which the constant B is calculated, only depends on the viscometer and the viscosity of the liquids.

8. *Barometric pressure*

As has been pointed out by Kooy and Hermans (7) the efflux time of the viscometer depends to some degree on the atmospheric pressure. The main error is caused by changes in the density of the air. It is relatively unimportant; for toluene a change of 5 mm Hg in the air pressure gives a change of the efflux time of about 1/100 second if the total efflux time is 1000 seconds.

It may be appropriate to point out that, for the viscometers which are totally enclosed in these experiments, a pressure error also may arise if there are temperature gradients when the viscometer is closed. This error is caused by two factors. Firstly due to the direct pressure increase with temperature (a difference of the temperature of 2° will give a pressure error of just about 5 mm Hg) and secondly to the change of the vapor pressure of the liquid in the viscometer when the temperature is changed. Both errors are of about the same magnitude when the "worst" liquids in this work

are used. These errors work in the same direction but, as the filling and the closing of the viscometer are always made in the room where the thermostat is placed and this room is thermostated to better than one degree (see p. 407), there is no risk that this temperature-pressure error will interfere with the measurements reported here. (When the viscometer is closed the air in the viscometer is always saturated with the vapor of the liquid used, see p. 419; if not, another pressure error would arise.)

9. *Adsorption*

The adsorption of polymer from the solutions used in the measurements causes at least three different errors.

Usually the concentration of the solution is determined by weighing, but then when polymer is adsorbed on the walls of both the bottles used and the viscometer, the concentration is decreased and the efflux times determined are too short when compared with the original concentrations (18). Thus the values of η_{sp}/c will be somewhat low. This error may be rather marked at very high dilution. To a certain degree it may be avoided if the viscometer is shaken with a part of the solution before the measurement. In a similar way it may also be reduced during the preparation of the solutions (see p. 418).

Another error due to adsorption is caused by the diminishing of the diameter of the capillary when the polymer is adsorbed. This error may greatly change the shape of the curve η_{sp}/c vs. c. The importance of this error has arisen in that work, but as two preliminary reports on the subject have already been published (11, 12), it will be discussed but briefly here.

It must be assumed that the molecules adsorbed to some degree at least retain the volumes and the shapes they have in the solution, if the reduction of the diameter of the capillary shall be great enough to change the efflux time to measurable extent. To calculate the influence of the high polymer layer adsorbed on η_{sp}/c we denote the apparent relative viscosity observed by η_r^*, the true relative viscosity by η_r, the capillary radius r and the thickness of the layer by a. Then we have

$$\eta_r = \eta_r^* \left(\frac{r-a}{r}\right)^4 = \eta_r^* (1 - 4\,a/r) + \ldots, \tag{8}$$

which gives

$$\eta_{sp}^*/c = \eta_{sp}/c + 4\,a\,(\eta_{sp}/c + 1/c) \cdot 1/r, \tag{9}$$

where η_{sp}^*/c is the apparent reduced viscosity and η_{sp}/c the true one.

For a given concentration a may be assumed constant and then, due to Eq. (9), we have a linear relationship between η_{sp}^*/c and $1/r$. Thus if we measure the viscosity at this concentration with capillaries with different diameters and plot η_{sp}/c against $1/r$, the intercept will give the true η_{sp}/c since the adsorbed layer at $r = \infty$ does not influence the efflux time. The suspended level viscometer has been constructed with three capillaries with different diameters (see p. 403) in order to extrapolate to $r = \infty$. (A similar Ostwald viscometer, fairly convenient when used, seems to be very difficult to construct.) The extrapolation is only permitted when the liquids are Newtonian, or if we work at about the same maximum gradient of velocity in all the capillaries. As mentioned, this latter condition has been arranged during the construction of the suspended level viscometer (p. 403). Thanks to this same maximum

gradient in all capillaries the mechanical deformation of the adsorbed layer due to the flowing liquid is very likely the same.

Since the publication of the preliminary reports on this adsorption error, further publications on the same subject have become available. They will not be discussed here, but in the last part of this work many of them will be discussed in connection with the presentation of some new results concerning this problem (p. 432).

The last error due to adsorption refers to the volume. The adsorbed layer will diminish the volume of the upper bulb. This error is not great but will perhaps now and then influence the results. Relatively it may be of the magnitude $1 - 2 \times 10^{-5}$ for S1 and about the double for S3. See also p. 426.

Part III

PREPARATIVE WORK AND THE ACTUAL MEASUREMENTS OF VISCOSITY

Chapter 5. General considerations

For our measurements we have used mainly two different types of molecules. (1) Statistically jointed chain molecules of the same kind but with different molecular weights. (2) Rigid linear macromolecules of different molecular weights in a good solvent to ensure that they are as elongated as possible.

As a suitable representative for the first polymer type polystyrene was chosen for several reasons. It is relatively easy to polymerize styrene and to fractionate the polymer obtained. Furthermore polystyrene is quite easy to work with, a fact which is very important in this case since the measurements in themselves are intricate. It also seems to be one of the most well-characterized synthetic high polymers and hence it is easy to make comparisons of different kinds; several of the works already published dealing with the problems in view are all made with polystyrene (3, 5, 7). As solvent toluene was chosen; this was also used in the references given above.

As a suitable polymer with rigid linear molecules nitrocellulose was chosen with ethyl acetate as the solvent.

Besides the measurements with the systems mentioned some other measurements have also been made. Linear polymethyl methacrylate was compared with a branched copolymer of methyl methacrylate and glycol dimethacrylate with ethyl acetate as solvent. Recently two different types of polyvinyl acetate, one linear and the other branched, were also investigated.

Chapter 6. Preparative work

The preparative work mainly consisted of making polymerizations and fractionations. For the characterization both of the crude polymers and the fractions, determinations of the intrinsic viscosities were made. Sometimes the sedimentation constants were also determined.

A. *Polystyrene*

1. *Polymerization*

Only some of the measurements with polystyrene will be discussed in detail in this paper and, for this reason, only the polymerization of styrene will be described exhaustively, whilst the work with the other synthetic polymers will be but briefly mentioned.

The styrene polymerization was made in bulk with benzoyl peroxide as initiator. The main objective in the preparation was to get fractions with different molecular weights in a rather wide interval and with the structure of the molecule as homogeneous as possible throughout all fractions. To do this it was considered best firstly to polymerize with a low concentration of initiator and at a low temperature and secondly to stop the polymerization at a relatively low degree of conversion.

The styrene used (Kebo, purum, 99–100 %, stabilized with *p*-tert-butylcatechol) was first set free from the inhibitor by washing twice with 10 % sodium hydroxide. Then it was washed three times with distilled water and dried with Drierite (white). Finally it was distilled twice in a column in an atmosphere of nitrogen at low pressure (70 mm Hg). The receiving vessels were cooled with ice.

The benzoyl peroxide used ("Benzoylsuperoxid, reinst, f. wissensch. Zw. Dr. Theodor Schuchardt, München, Germany") was first recrystallized from chloroform (LKB, pro analysi). Then it was dissolved in acetone (Merck, pro analysi), and sufficient distilled water was slowly added to cause about half of the peroxide to reprecipitate. The precipitate was placed on a fritted glass filter and dried in vacuum at room temperature.

The middle fraction obtained in the second, relatively rapid distillation of the styrene, was distilled directly into a glass ampoule with 2.3 cm inside diameter and with a length of 42 cm. It was filled to about $\frac{9}{10}$ of its volume. The total amount of benzoyl peroxide was calculated (with respect to a suitable degree of conversion) to be only 4.71 mg. Since its weight ought not to differ too much from this value, it was suitable to measure this amount volumetrically. The correct portion of a dilute solution (in methyl ethyl ketone) with known concentration was introduced in the ampoule. The solvent was evaporated after which the styrene was distilled (the ampoule was then cooled with ice as already mentioned), and finally the ampoule, cooled with dry ice and evacuated (about 0.5 mm Hg), was closed. When the frozen styrene had melted again the ampoule was shaken a little until the peroxide was dissolved and put into a thermostat with a temperature of 58°C. With the thin ampoule the temperature of the polymerizing system ought not to have risen appreciably above the temperature of the thermostat. The polymerization time, 55 hours, had been chosen so that a degree of conversion of only about 10 % was to be obtained. To stop the polymerization the polymerizing system was poured into cooled methanol,

Table 2. Polymerization data for polystyrene.

Styrene, weight in g	155.6
Polystyrene, weight in g	13.4
Degree of conversion, %	8.6
Benzoyl peroxide, % by weight	0.003
Temperature of polymerization, °C	58
Time of polymerization, hours	55
Intrinsic viscosity, $[\eta]$, of the crude polymer, ml/g (in toluene)	280

so that the polymer was precipitated, and then almost immediately the precipitate was taken on a filter and carefully washed with methanol. The precipitate was dissolved in methyl ethyl ketone (5 %) and the solution, while being stirred, was slowly poured into the same volume of methanol and after 2 hours the precipitate was taken on a filter, washed with methanol, and dried in vacuum at room temperature.

A comprehensive list of data for the polymerization is given in Table 2.

2. *Fractionation*

Here, for the same reason as in 1, only the fractionation of polystyrene will be described. The method of precipitation was used. It seemed best to get the polystyrene ($\sim$13 g) obtained in fractions, the weights of which should not be considerably lower than 0.5 g and not higher than 1.5 g. About twenty fractions were desired. Thus the weight should normally be lower than 1 g. To get a result as good as possible with a reasonably small amount of work it was decided to use successive precipitations according to the principle recommended for instance by Flory (28) and Boyer and Simha (29). In each precipitation from the main solution a somewhat larger fraction than desired is obtained and this fraction is then redissolved in a rather large amount of solvent and precipitated again to a suitable degree from a more dilute and thus also a more appropriate solution than the main one. When that second precipitate is filtered off the rest of the polymer in this dilute solution is also precipitated and returned to the main solution to which a little solvent is added so that all the polymer redissolves. This method permits one to work with small volumes but nevertheless the fractions are obtained from very dilute solutions.

Methyl ethyl ketone was used as solvent and methanol as the precipitating agent. An original concentration of the main solution of about 0.5 % was considered as suitable; in all 2.7 l methyl ethyl ketone was used. When methanol (330 ml) had been added to the solution until a slight turbidity was obtained, the solution was heated so that the temperature rose from 25° to about 35°. An additional 12 ml of methanol (the amount determined from a previous experiment) was added and then the solution allowed to cool slowly (during $\sim$10 hours) to 25°. The solution was stirred during this time. At 25° the stirring was stopped and the precipitate was allowed to settle.

In fractionation work we always worked with enclosed flasks in order to avoid vaporization. For the stirring in these flasks a special stirrer, described in another paper (30) was constructed. It functioned satisfactorily, and especially the simple shape of the part dipping into the liquid, in reality consisting of a straight glass rod, was important as almost no precipitate fastened to the same. Only when precipitating the last low molecular weight fractions was there any indication of polymer on the rod, but this was easy to remove.

Table 3. Fractions of polystyrene.

Fraction No.	Weight g	$[\eta]$ ml/g (toluene)	$\overline{M}_v$
4	1.1	470	2,500,000
12	0.5	214	800,000
18	0.4	118	300,000

When a few fractions had been obtained it was necessary to increase the amount of methanol added per fraction to get a suitable amount of the precipitate. In the same manner the temperature must be increased to 40° in order to prevent precipitating when the methanol was first added. In all, 20 fractions were obtained. For their characterization their intrinsic viscosities were determined. For this work an Ubbelohde viscometer of the dilution type was used. Weights and intrinsic viscosities of the three fractions used in the following measurements are given in Table 3.

B. *Nitrocellulose*

The nitrocellulose used was kindly placed at our disposal by Dr. A. G. Chitale. Besides the viscosity measurements made by the present author some other measurements both by Dr. Chitale and others have been made with these same samples at this Institute. It was considered best to make measurements partly with a rather highmolecular and partly with a more normal fraction.

The nitrocellulose was prepared by cotton nitration. A determination of nitrogen content gave the value 13.87 %. (The analyses were carried out at the Central Analytical Laboratory, Uppsala University.) For the fractionation the precipitation method had been used. Acetone was the solvent and water the precipitating agent. The fractions were dried in vacuum (nitrogen atmosphere) at ~60°C. Some data for the fractions used here are given in Table. 4.

Table 4. Fractions of nitrocellulose.

Fraction No.	$[\eta]$ ml/g (ethyl acetate)
2	880
6	405

Chapter 7. Measurements of the viscosity

A. *Preparation of the solutions*

1. *Polystyrene*

After the preparation, the polystyrene was stored for several months in a vacuum desiccator. The last 24 hours before the solutions were prepared the desiccator was evacuated with a forepump to a vacuum less than 1 mm Hg. A trap between the pump and the desiccator was cooled with a mixture of dry ice and chloroform.

The solvent was redistilled about a week before it was used. In that way variations of its properties with time surely should have passed the relatively rapid intitial stage before the solutions were prepared. It was desirable to keep the moisture content rather constant and of a relatively low value. Before the distilling the solvent was first dried carefully (with Drierite) and afterwards stored in special flasks from which suitable portions could be pressed out with dry air. (This operation lasted for less than a minute and the additional pressure was slight so that the risk of dissolving much air was negligible.) Further intricate procedures to avoid absorption of moisture from the air during the preparation of the solutions were not made.

The concentrations of the solutions were usually determined by weighing. The

most diluted solutions were obtained by dilution from stock solutions in one or two steps. To reduce the concentration error, due to adsorption, as much as possible for the most diluted solutions where its effect may be rather great, the dilutions were made in the following way. Usually the last 5 to 6 solutions were obtained from the same stock solution. This solution was first divided into 5 to 6 equal parts and each poured into a weighed separate flask. The flasks were then shaken carefully from time to time with the solutions stored in them. After 3 to 4 hours all solutions were poured back into the stock solution flask and shaken together. Then adequate portions of the stock solution so treated were poured into the flasks already rinsed with the solution, weighed and diluted with pure solvent. This procedure changed the concentration of the stock solution a little (evaporation and adsorption working against each other), but at the same time the concentration was almost exactly the same for the stock solution portions in the different flasks, and there were no adverse adsorption effects when most dilute solutions were prepared.

Both theoretical determinations and experimental test showed that the errors in the concentration apart from those due to adsorption were barely higher than $\frac{1}{2}$ % at any time, and usually they were much lower. By following a fixed procedure for the preparation of the solutions the errors were probably rather equal in value for the different solutions and of the same sign. Thus their importance for the measurements in question was largely eliminated; a pervading, smaller error in the concentration will not change the shape of the curve η_{sp}/c vs. c very much but only its position. Usually the volume of the solutions prepared was about 100 ml. The solvent was added the polystyrene and left for twenty-four hours, during which time it was shaken repeatedly. The final diluted solutions were also not used for twenty-four hours. After preparation, the solutions were stored in closed flasks in a box where the moisture was removed with calcium chloride. Usually some ten solutions were prepared for every measurement on a fraction. The concentrations were chosen so that the most diluted one gave an η_{sp} of ~ 0.001, whereas the concentrations of the rest usually were distributed to give η_{sp} between this value and 0.1. The pure solvent used in the series of measurements to obtain t_0 (efflux time of solvent) was manipulated in a similar way and stored in closed flasks as were also the solutions.

2. *Other polymers*

Usually the solutions of the other polymers were prepared in a manner analogous to that described for polystyrene. But especially with the nitrocellulose some further precautions against degradation had to be taken. The nitrate was stored in methanol and dried over night in vacuum before the preparation of the solutions which were then stored in the dark.

B. *The measurements of viscosity*

1. *Cleaning of the viscometer*

After the measurement of a polymer fraction, the viscometer was first rinsed repeatedly with a good solvent for the polymer. The solvent had to work for many hours and in that way the adsorbed polymer was removed to a large extent. Then, eventually via a second solvent completely soluble in both the solvent first used and water, the viscometer was rinsed with water. For the following cleaning of the viscometer we usually used a mixture of sulfuric, hydrochloric and nitric acids in water. The mixing was made in the viscometer in order to obtain an evolution of heat. This acid mixture

was usually employed for twenty-four hours and then the viscometer was rinsed repeatedly with water and with ethanol, which was left for at least two hours. Finally it was washed repeatedly with the solvent which was to be used in the following measurements. All the liquid was filtered into the viscometer through a filter G4. Such cleaning was only made when the measurements of a complete fraction were finished, or under special circumstances.

2. *Filling of the viscometer*

The measurements of a polymer fraction were made in such a manner that the efflux time of the viscometer for pure solvent was first determined and then the efflux times for the different solutions in order of increasing concentration. Due to the above the cleaning was completed by carefully rinsing with the solvent, which was to be used in the following measurements. Then, as the volume of liquid in the viscometer might fluctuate within relatively wide limits, it was not necessary to dry the viscometer after the cleaning, but it could be allowed to immediately filter the solvent into the same. A special sintered-glass filter funnel, which was connected to the opening of the viscometer with a ground (glass) joint, was used. The liquid was pressed through the filter by means of a diminutive excess of pressure. Then the viscometer was closed according to chapter 3 (p. 404). As an additional guarantee for waterproof closing a layer of picein lacquer was put on at the ends of the rubber tube. When changing from solvent to solution and to still more concentrated solutions, the original liquid was first carefully emptied, the viscometer was rinsed twice with 15–20 ml of the solution to be used at the next measurement, and then finally it was filled with the solution. The part of the liquid that was impossible to pour out from the viscometer did not exceed $\frac{1}{2}$ ml, and as the filling volume was not below 50 ml, the concentration error due to this dilution was surely not high enough to influence the results obtained even in the most extreme case. Thanks to this repeated rinsing with solution some other advantages were gained. In this way the filter funnel was rinsed with solution so that it was possible for the filter to adsorb high polymer molecules to a rather high extent before the part of the solution to be used in the measurement passed through the filter. In this way its concentration was surely reduced but little due to adsorption in the filter. In the same way it was possible to get an adsorption layer on the walls of the viscometer (probably not complete) before the final solution was poured in.

3. *Measurements*

After the viscometer was filled with liquid it was placed in the thermostat. A thermostating time of about half an hour was always sufficient for a constant temperature to be attained. But it was found that it was necessary to wait about one hour until the adsorbed layer on the walls of the viscometer was almost in equilibrium with the solution. For that reason the viscometer was always held in the inverted position for at least one hour after that the "upper" bulb (*A*, Figs. 2 and 3, pp. 403, 404) and the capillary were filled and possible air bubbles in the capillary removed by means of a temporary forcible tilting. The suspended level viscometer was then ready for measurement. The Ostwald viscometer on the other hand was first placed in a horizontal position and the volume to be used in the measurement adjusted as earlier described (p. 402). After this adjusting it was held in that position

for a further ten minutes and then it was put in position for measurement. In the following measurements the Ostwald viscometer was held in the inverted position for 15 minutes and for 10 minutes in the horizontal position. These times were chosen to have the drainage as small as possible (p. 410).

The measurement of the efflux time was made as previously described (p. 407).

Part IV

RESULTS, DISCUSSION AND CONCLUSIONS

Chapter 8. Results from measurements with the highest precision obtainable

From the experience with some preliminary measurements it was obvious that the middle fraction of polystyrene in toluene would give the solutions that were most suitable for measurements with the highest precision. For these the suspended level viscometer with three capillaries was chosen. The diagrams obtained from one of these series of measurements are given in Figs. 5 and 6.

Fig. 5 comprises the whole concentration interval, whereas Fig. 6 shows in detail the conditions at very low concentrations only. In addition to the η_{sp}/c values that are corrected also for the adsorption effect, as described in Chapter 4, p. 413, the uncorrected values of η_{sp}/c have been plotted versus c. Primary data for these diagrams are given in Table 5. (It may be observed that the relatively great change of the efflux times for the lowest concentrations does not mean that the true η_{sp}/c is changed by a corresponding amount, as we have a similar change for all the three capillaries.) The slope of the curve gives the value 0.3 for k' in Huggins' equation (p. 399).

When going to discuss the diagrams we must first emphasize that for this polymer-solvent system the "critical concentration", according to Boyer and Spencer (13), that means the concentration corresponding to the hexagonal close-packing of spheres with diameters two times these obtained for the random coils of the molecules

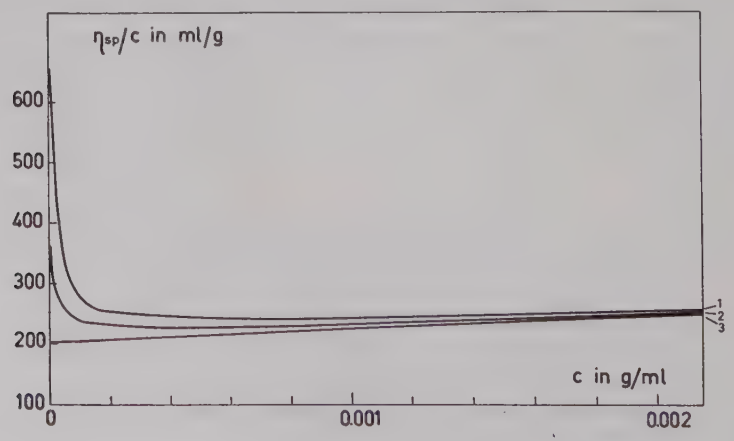

Fig. 5. Viscosity of polystyrene in toluene. True $\eta_{sp}/c = f(c)$, 3, and uncorrected $\eta_{sp}/c = f(c)$, 1, 2. (The curve from S2 is omitted.)

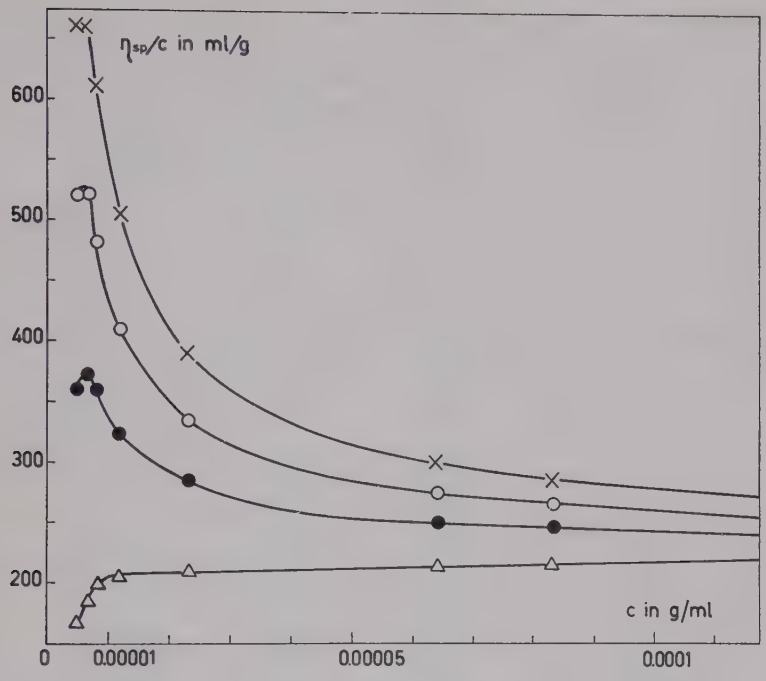

Fig. 6. Viscosity of polystyrene in toluene. True $\eta_{sp}/c = f(c)$, △. Uncorrected $\eta_{sp}/c = f(c)$: ●, for $d = 0.5$ mm; ○, for $d = 0.3$ mm; ×, for $d = 0.2$ mm.

in question in the actual solvent was estimated to 0.0003 g/ml. Then we choose for our discussion an interval of concentration from 0.00001 g/ml to 0.002 g/ml or from a concentration 30 times lower to a concentration 7 times higher than the calculated "critical" one. In spite of the fact that we thus surely have the "critical concentration" in the interval investigated, there are no greater deviations from the linear curve obtained by plotting the true η_{sp}/c vs. c. It is evident from the curves and the primary data that the accuracy is very high in this interval.

A critical examination of the curve will but show that there is a very small "upward convexity" already at concentrations of about one third of the "critical" one. But still at concentrations thirty times lower than this the deviation from the above straight line is not greater than that which would correspond to a decrease of η_{sp}/c of two per cent. If the change in slope at these concentrations much lower than the "critical" one, is real, it would mean a certain experimental confirmation of the theories of Simha (1) and of Riseman and Ullman (2). But we must observe that the correction to be applied to the uncorrected η_{sp}/c value obtained with the S1 viscometer is very great at concentrations beneath 0.0001 g/ml and an error of only a few per cent of that correction is enough to change the slope of the curve with several hundred per cent. For this reason it is impossible to decide if there is a change in slope of the true viscosity curve.

For the middle fraction of polystyrene in toluene here investigated it is first at concentrations 50–100 times lower than the "critical" one as accidental errors become

Table 5. Efflux times of solutions of polystyrene fraction No. 12.

Concentration g/ml	Efflux times in s		
	S1	S2	S3
0	881.52	1532.80	1112.14
	51	83	12
	48	80	13
	51	80	10
	51	81	12
	53	81	09
0.00000470	882.89	1536.52	1115.50
	99	59	60
	883.07	69	69
0.00000631	883.54	1537.70	1116.64
	55	75	67
	62	82	76
0.00000761	883.93	1538.40	1117.27
	93	48	25
0.0000118	884.88	1540.10	1118.69
	91	15	75
0.0000232	887.29	1544.64	1122.21
	31	65	23
0.0000567	893.98	1556.57	1131.06
	97	64	09
0.0000732	897.36	1562.60	1135.54
	37	57	53
0.000145	911.72	1587.74	1153.99
	71	74	1154.00
0.000230	928.61	1617.37	1175.62
	63	37	63
0.000552	995.15	—	1260.43
	12	1733.65	44
0.000865	1060.35	1847.40	1342.84
	33	38	90
0,00134	1166.02	2031.81	1477.52
	1165.99	85	48
0.00196	1315.50	2292.90	1667.40
	49	88	38

noticeable. The difficulties encountered are formidable here. The time difference for solution and solvent is not greater than 0.1 per cent of the efflux time. This means that a relative error of 0.01 per cent in efflux time will give an error of ten per cent in η_{sp}/c. Though outside the scope of this work it may be of some interest to discuss the viscosity curve at these concentrations below the concentration interval now discussed. In Fig. 6 there is an indication that the curve might "bend down" here at the lowest concentrations. A similar "bending down" has been observed many times (see also Fig. 7). But with the high corrections here due to adsorption it is very difficult to decide definitely if the "bending down" is real. The correction which must be made to the value of η_{sp}/c obtained from S1 (see p. 413) is in any case several times the difference between the true η_{sp}/c and the value that corresponds to an extra-

polation of the linear curve. It is also possible that the assumption for the correction that the effective layer is of the same thickness for all capillaries is not quite valid here where the adsorption is very small. Much can be said in favour of a "bending down" of the curve. Firstly an evident tendency to a "bending down" has been obtained. Under no circumstances is there a "bending up". This effect occurs in spite of the fact that attempts have always been made to prevent as well as possible a "bending down" due to different experimental errors; the shortest conceivable efflux time for the solvent has been used and the dilution method ought to guarantee that the concentration is not diminished, etc. But there are many sources of error which work for a "bending down". One of the most serious is the decrease in concentration due to adsorption and another the reduction of the viscosity due to absorption of water. Others are degradation of the polymer molecules and higher adsorption in the finer capillaries than in the wide one (the solution is often in contact with these finer capillaries for a longer time than with the wider one), so that the corrections are too high.

A fact that may be noted is that in nearly all the measurements "the bending down" of the extrapolated curve appears at a concentration where the curves which are not corrected for adsorption have a maximum. Leaving pure errors of measurement out of the question, this maximum must be caused by one or both of the following reasons: (1) The adsorption isotherm bends down to quite a large extent at concentrations lower than that of the maximum, so that for these concentrations $da/dc > a/c$, if a is the thickness of the apparent adsorption layer. (2) We have a rapid reduction here in the true value of η_{sp}/c. Much is to be said in favour of a real "bending down" of the true viscosity curve, but there are also indications that sometimes the condition above of the adsorption, $da/dc > a/c$, may be fulfilled (see p. 429). A simultaneous appearance of these two effects is perhaps more than a coincidence. If there is indeed a change in the viscometric behaviour at this extreme dilution, as may be indicated by the "bending down" of the extrapolated curve, it is not imposible that there is also another effect of the same nature that may be observed here. The course may be the following. If the viscosity increases rapidly the hydrodynamic action on the adsorbed layer must increase very much (we have the maximum gradient here). Hence it is possible that in that interval of concentration where the adsorbing surface is perhaps not totally covered by polymer molecules, the adsorption is rendered more difficult. On the other hand at higher concentrations with a stronger adsorption this effect may be diminutive. (See also p. 429.) This would mean that the two eventual effects are both hydrodynamic in nature. Finally it must be pointed out again that the intention of the measurements now performed was not to investigate this interval of concentration and thus it is impossible to explain this behaviour with any certainty.

About the possibility to investigate still lower concentrations some brief comments may be made. It seems almost impossible to reach concentrations essentially lower than those now examined, due to the fact that many errors, earlier of minor importance, will now be significant. At the same time many correction terms become so large that the corrected values of η_{sp}/c at best can only be approximate. Even if some of the best improvements are tried it is doubtful if more pertinent information will be obtained. Such improvements include use of wider capillaries, use of more suitable polymer-solvent systems mainly with low adsorption and a series of measurements with decreasing concentration to ensure complete adsorption before the solution to be used in the actual measurement is poured into the viscometer. It must

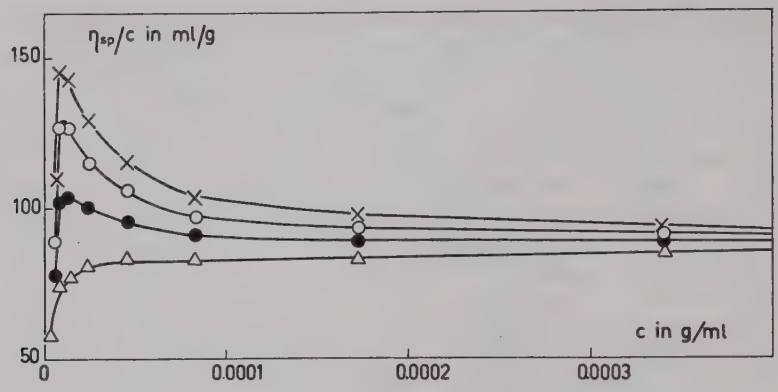

Fig. 7. Viscosity of polyvinyl acetate in toluene. True $\eta_{sp}/c = f(c)$, △. Uncorrrected $\eta_{sp}/c = f(c)$: •, for $d = 0.5$ mm; ○ for $d = 0.3$ mm; × for $d = 0.2$ mm.

also be remembered that all these improvements will greatly increase the time for a series of measurements which is at present about one month.

As the results obtained here are in many respects quite different from those given in the most interesting recent paper, published by Tuijnman and Hermans (8), a comparison between their data and ours will now be made. They examined polyvinyl acetate dissolved in toluene. Among other things, the dependence of the gradient on viscosity was studied. They believe that their measurements have shown that the anomalous viscosity curves are primarily due to non-Newtonian effects. This is not confirmed by our measurements. We have also made a few measurements with polyvinyl acetate–toluene solutions though primarily for investigations of other problems than those here mentioned (see p. 432).

The polyvinyl acetate used was kindly placed at our disposal by Dr. F. W. Peaker, Chemistry Department, University of Birmingham, Birmingham, England. The samples we have received are two of the fractions he described at the Macromolecular Symposium in Prague, 1957 (31); a branched fraction under the code number SM in reference 31 and a linear fraction used as "backbone" in the preparation of the branched one. Their data are given in Table 6.

For this first comparison with the results of Tuijnman and Hermans only the measurements with the linear fraction are of any interest.

From Fig. 7 it is clear that the diagram of this polyvinyl acetate fraction is essentially equal to that of polystyrene. The extrapolated curve is linear down to concentra-

Table 6. Fractions of polyvinyl acetate.

Sample No.	Frequency of branching in number of branches per 1000 monomer units of "backbone"	$[\eta]$ (tetrahydrofuran) in 100 ml/g	Huggins' constant k'
SM	2.14	1.790	0.53
SM "backbone"	—	1.335	0.33

tions much lower than the lowest one examined by Tuijnman and Hermans. The thickness of the adsorbed layer in our viscometer is about 500 Å at a concentration while they report a value tenfold higher. Tuijnman and Hermans have also determined the adsorption directly and then they obtained the very high value of about 0.01 mg/cm². This means that they have a polymer concentration of approximately 0.2 g/cm³ in the adsorbed layer. Unfortunately no results of adsorption of polyvinyl acetate on glass, besides these mentioned, seem to have been published. But results for other similar polymers such as polystyrene, polymethyl methacrylate and polyvinyl chloride have been published by Jenckel and Rumbach (32) and Fendler, Rohleder and Stuart (33). The values given in these papers are only about 0.0015 and 0.0003 mg/cm² respectively. Even if these two values are very different from each other they are definitely lower than the result of Tuijnman and Hermans. A thickness of 5000 Å would further necessitate a layer at least 5 molecules thick even if they are not deformed at all. This value seems rather high. Thus the values of Tuijnman and Hermans for the adsorption are perhaps too high. But then it is necessary to ask if the curve (see Fig. 4 in ref. (8)), on whose shape this calculated thickness is somewhat dependent, is correct. If we assume a more reasonable value for the thickness, the S-shape of the curve will probably be essentially less accentuated. This would also mean that the gradient dependence is essentially smaller than stated. The S-shaped curve seems moreover to mean that an important part of the total decrease in viscosity with increase of the shearing stress (zero to infinity) occurred over a very

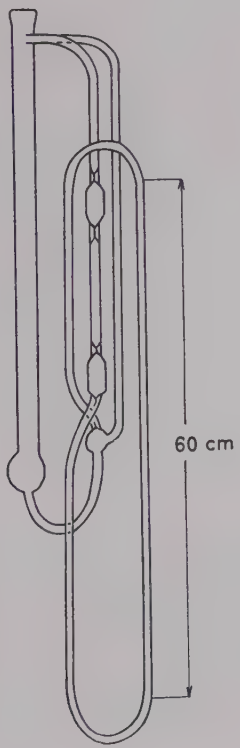

Fig. 8. Viscometer for two different gradients.

limited interval, i.e. $0.4 - 1.6$ g cm^{-1} s^{-2}. This is in opposition to all experience of this Institute and for this reason we have made an effort to determine if our polyvinyl acetate behaves in a similar manner. We have not aspired to make a systematic study of the gradient dependence, as Tuijnman and Hermans did, but to examine a solution with two different gradients which are equivalent to the highest and lowest values that the above authors used. From such a study it is possible to obtain the total gradient dependence of the viscosity in the interval in question. The dependence found by Tuijnman and Hermans was about 1 % of the viscosity. Such a great change of viscosity is very easy to observe. But efforts have to be made to ensure that it is a *gradient dependence* and *no other effect* which is determined. A modified Ubbelohde viscometer has been constructed and is shown in Fig. 8. It has two bulbs to permit measurements to be made at two different gradients. A list of its dimensions and constants is given below:

Capillary length, 150 cm
Capillary diameter, 0.03 cm
Mean hydrostatic head, 30 and 7 cm
Max. shearing stress (toluene), 1.3 and 0.3 g cm^{-1} s^{-2}
Efflux volume, 3 and 3 ml
Efflux time (toluene), 5000 and 21,000 s

Measurements have been made at the concentration 0.0009103 g/ml. The relative viscosities obtained are 1.0787 and 1.0790 for the highest respectively lowest gradient. It is clear from the results that, within the limits of error, no gradient dependence may be observed. A critical examination of the possible errors that may be serious in these measurements shows that both drainage and surface tension errors surely are greater in the measurements of Tuijnman and Hermans than in ours. They use a much smaller bulb, lower mean hydrostatic head, and must have an external pressure for higher gradients. Thus it seems certain that the gradient dependence of our solution is not higher than about one tenth of the value they reported. Of course it must be emphasized that the molecular weight of our sample is lower than that of the fraction used by Tuijnman and Hermans. The intrinsic viscosities are 80 ml/g and 130–140 ml/g respectively. But this difference alone cannot explain the very different results. In any case we may surely conclude that in the system polyvinyl acetate-toluene now examined the anomalous viscosity concentration curves are due only to adsorption and not to non-Newtonian effects.

It may be pointed out here that with the thickness of the adsorbed layer given by Tuijnman and Hermans, the relative reduction of the volume of their very small viscometer bulb is great enough to explain the fact that their viscosity curve on the whole has a very marked "upward convexity". This behaviour has never been observed in any of our measurements.

Summing up what has been said here it is evident that: (1) All the anomalies that have been observed in this actual concentration interval around the "critical concentration" are only due to the fact that no correction of adsorption effects have been applied. (2) The true viscosity curve is perfectly linear through this interval of concentration but at concentrations much lower than the "critical concentration" there is some evidence of a "bending down" of the curve.

Chapter 9. A brief presentation of the measurements with different fractions of polystyrene and nitrocellulose

Figs. 9–13 show the diagrams η_{sp}/c vs. c obtained from measurements with polystyrene in toluene and nitrocellulose in ethyl acetate. The diagrams in Fig. 9 are from measurements with the suspended level viscometer.

From Figs. 9–11 it is obvious that for the different polystyrene fractions we always have the usual type of "viscosity curves" when no corrections for the adsorp-

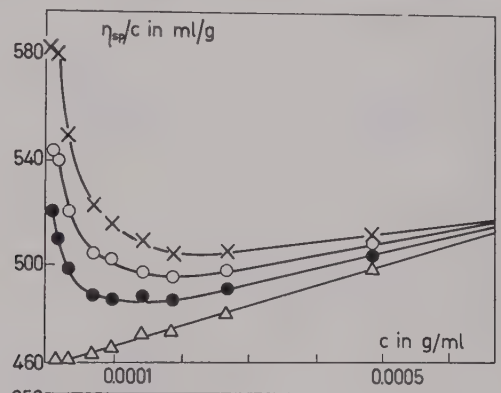

Fig. 9. Viscosity of polystyrene (No. 4) in toluene. (Suspended level viscometer with three capillaries.) True $\eta_{sp}/c = f(c)$, △. Uncorrected $\eta_{sp}/c = f(c)$: ●, for $d = 0.5$ mm; ○, for $d = 0.3$ mm; ×, for $d = 0.2$ mm.

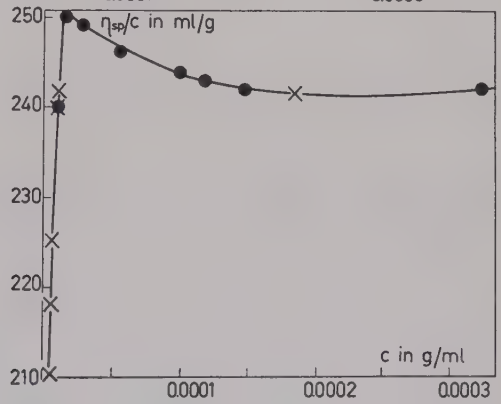

Fig. 10. Viscosity of polystyrene (No. 12) in toluene (Ostwald viscometer).

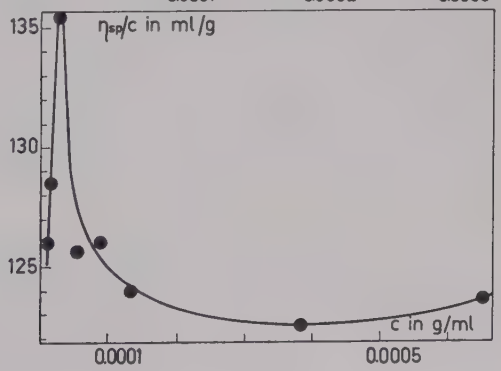

Fig. 11. Viscosity of polystyrene (No. 18) in toluene (Ostwald viscometer).

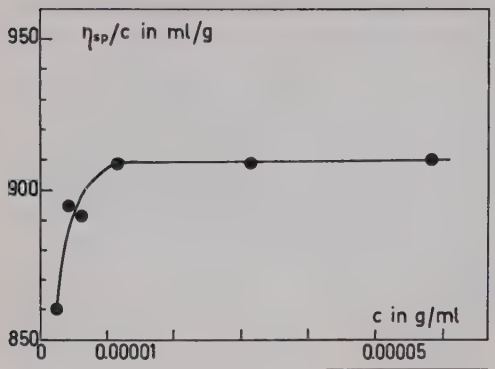

Fig. 12. Viscosity of nitrocellulose (No. 2) in ethyl acetate (Ostwald viscometer).

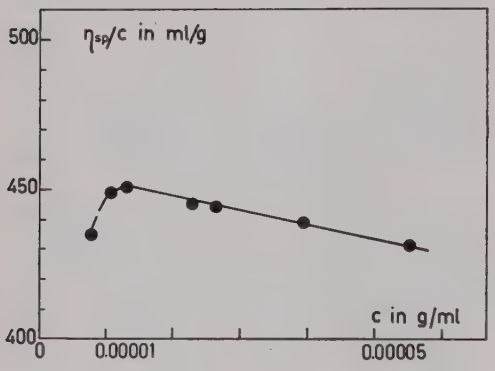

Fig. 13. Viscosity of nitrocellulose (No. 6) in ethyl acetate (Ostwald viscometer).

tion effect are applied. The concentrations of the obtained minima are at least qualitatively in agreement with the conditions of Eq. (4) in reference 12 which gives the concentration dependence of the minimum, assuming that it is due to an adsorption. It may also be observed that the magnitude of the radius of curvature changes with the molecular weight qualitatively as Eq. (5) in the same reference states. The very abruptly "bending down" of the curves of fractions Nos. 12 and 18 may be observed. For fraction No. 12 the lowest concentrations have been reinvestigated with solutions obtained from a new stock solution. The two series agree very well.

The most interesting fact of the nitrocellulose diagrams in Figs. 12 and 13 is that the maxima of the curves are not as marked as those of the polystyrene curves. This may be due to a smaller thickness of the adsorbed layer of the rodshaped nitrocellulose molecules than of the coiled polystyrene molecules; about the same explanation as may be given for the different results of Batzer (19) for linear and branched molecules (see p. 432). Higher degradation of the nitrocellulose may be another explanation.

Chapter 10. Adsorption isotherm, obtained from viscosity measurements

As has been mentioned in one of the preliminary reports (11) it is possible to determine the thickness a from the uncorrected η_{sp}/c values obtained with the different capillaries. We wish to discuss the diagram a vs. c, i.e. the adsorption isotherm that

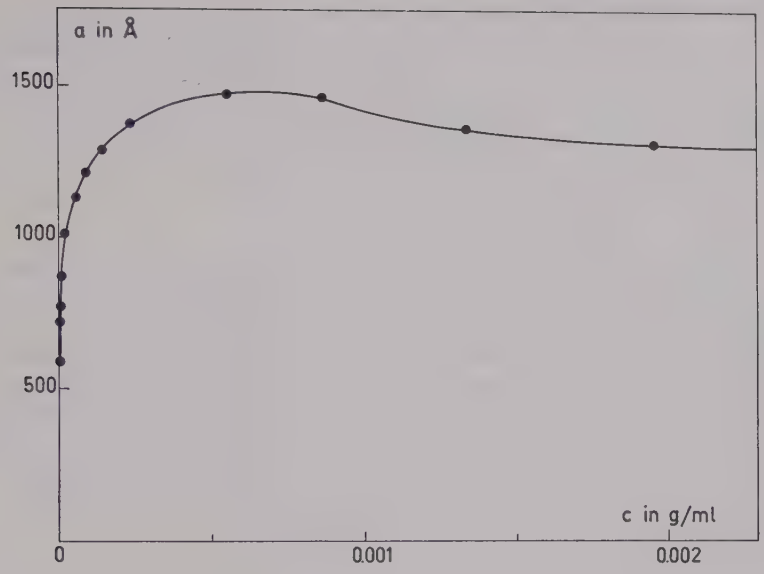

Fig. 14. Adsorption isotherm for polystyrene (No. 12) in toluene. $a = f(c)$.

corresponds to the viscosity curves of Figs. 5 and 6. Fig. 14 gives this adsorption isotherm.

We see that the magnitude of a corresponds to an adsorbed layer of the order of one or two molecular diameters in thickness. This is of about the same order as given in the preliminary report. An examination in detail of several adsorption isotherms has shown that at the lowest concentrations there is a small indication that $da/dc > a/c$. This might explain the maximum of the uncorrected viscosity curve. The reasons for this rapid reduction of the adsorption with concentration may be that at these extremely low concentrations when the adsorbing surface has not yet been totally covered with adsorbed molecules, the hydrodynamic action on the adsorbed molecules is relatively high and thus the total adsorption diminishes further. (See also p. 423.) In reference (11) it was indicated that there was a tendency for a to decrease with an increased concentration, when a concentration of 0.001 g/ml was reached. This seems to be verified now. A possible explanation of this reduction in a is that the molecules are not so expanded when the concentration increases. The maximum of the isotherm is obtained at the concentration where the effective volume of the newly adsorbed polymer balances the compression. It may be of some interest to compare the experimental compression curve with that theoretically estimated.

The concentration dependence of the expansion factor α is determined theoretically by Kawai (34) and Krigbaum (35). The formula derived by the latter is

$$\alpha^5 - \alpha^3 = \frac{C_M M^{\frac{1}{2}} (1/v_1 - 2\chi_{12})}{1 + x v_2 (1/v_1 - 2\chi_{12})} \left\{ 1 - \frac{2 C_M M^{\frac{1}{2}} v_2/\alpha^3}{1 + x v_2 (1/v_1 - 2\chi_{12})} + \cdots \right\} \qquad (10)$$

Here C_M is a constant

$$C_M = (27/2^{\frac{5}{2}} \pi^{\frac{3}{2}}) (\bar{v}^2/N V_1) (M/\overline{r_0^2})^{\frac{3}{2}};$$

$\bar{v}$ is the partial specific volume of the polymer, N the Avogadro number, V_1 the molar volume of the solvent, $\overline{r_0^2}$ the unperturbed mean-square displacement between chain ends, x the ratio of the molar volumes of polymer and solvent, v_1 and v_2 the volume fractions of the solvent and the polymer, and χ_{12} the interaction parameter characteristic for a given polymer–solvent pair at a given temperature. According to Kawai and Saito this may be approximated (36) to

$$\alpha^3 = 1 + (\alpha_0^3 - 1)/\{1 + (1 - 2\chi_{12})x\bar{v}c\}, \tag{11}$$

where α_0 is the value of α at $c = 0$.

We calculate the concentration dependence of a linear molecular dimension that has the same magnitude as a at the concentration 0.001 g/ml (we very approximately estimate the dimension of the adsorbed molecule to be the same as that of the molecule in solution). With $\alpha_0^3 = 3.10$ and $(1 - 2\chi_{12})x\bar{v} = 1600$, which values are approximately valid for polystyrene in toluene ($\bar{M}_v = 800{,}000$), we obtain the dotted line in Fig. 15, whereas the full line is the adsorption isotherm as given in Fig. 14. As the concentration $c_1 = 0.001$ g/ml is almost fifty per cent higher than the concentration of the maximum, it may perhaps be assumed that the adsorption has reached saturation at the concentration interval examined, so that the adsorption isotherm really gives the compression of the molecules. If we compare the values at two concentrations we have:

$$c_1 = 0.001 \text{ g/ml}, \quad a_1 = 1420 \text{ Å}, \quad \alpha_1^3 = 1.81$$
$$c_2 = 0.002 \text{ g/ml}, \quad a_2 = 1310 \text{ Å}, \quad \alpha_2^3 = 1.50$$
$$a_1/a_2 = 1.08, \quad \alpha_1/\alpha_2 = 1.06$$

Although the agreement between the two curves is quite good,[1] it is impossible from this comparison alone to obtain any further information about these phenomena. This would need a careful estimation of the concentration of the adsorbed layer and a theoretical calculation of the change of its thickness with concentration. On the other hand if such measurements may be assumed as adequate for the determination of the expansion of molecules it is easy to perform some improvements of the experimental methodics.

It may be pointed out that to be able to calculate the value of a with any accuracy at these relatively high concentrations the Eq. (2) does not approximate the "kinetic energy" correction with the desired accuracy. Schurz (37) has given the correct expression of the correction,

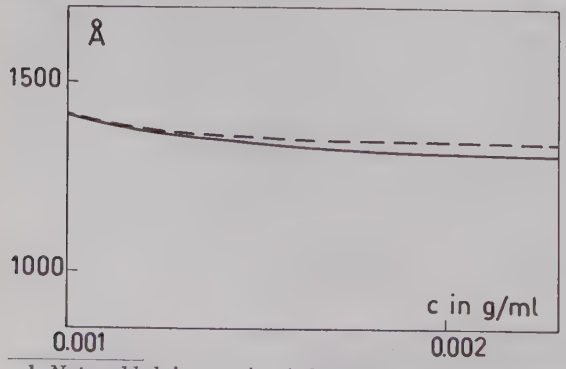

Fig. 15. Adsorption isotherm at higher concentrations (—), and the concentration dependence of the expansion factor (------). $a = f(c)$ and const. × $\alpha = f(c)$.

[1] *Note added in proof.*—A better approximation than that of Kawai and Saito will give a still better aggreement between the two curves.

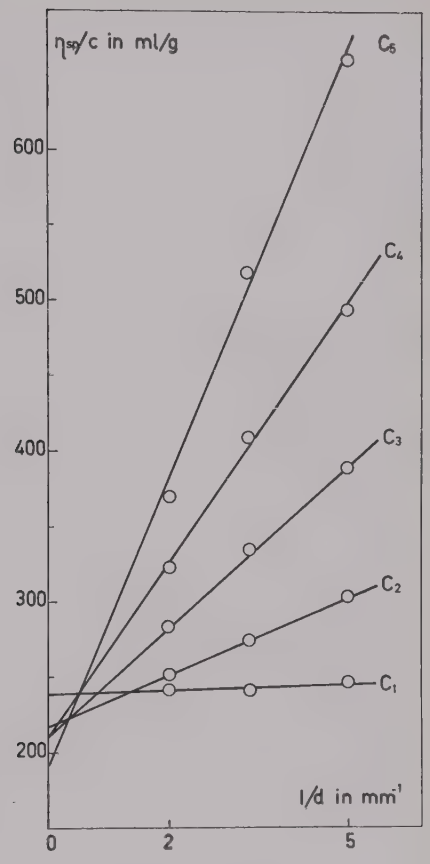

Fig. 16. Diameter dependence of uncorrected η_{sp}/c values. $c_1 = 0.00134$, $c_2 = 0.0000567$, $c_3 = 0.0000232$, $c_4 = 0.0000118$ and $c_5 = 0.00000631$ g/ml.

$$\eta_{sp} = \{\eta_{sp}\}\left(1 + \frac{t t_0^2 + B t_0}{t t_0^2 - B t}\right). \tag{12}$$

But this is here approximated to

$$\eta_{sp} = \{\eta_{sp}\}\left(1 + B\frac{t_0 + t}{t t_0^2}\right) \tag{13}$$

which may be used at the highest concentrations if the value of B/t_0^2 is not exceptionally high (the approximation is indeed better at higher concentrations).

Finally Fig. 16 shows some diagrams, used for the calculation of a, where the η_{sp}/c values are plotted versus the reciprocal of the diameter of the capillary, $1/d$. The graphs are practically straight lines down to the lowest concentration where a slight "upward convexity" may be observed. Hence we have quite good experimental consistency with the claims of the hypothesis (p. 413), that the diameter of the capillary is diminished a little due to adsorption.

Chapter 11. A comparison between the present results and some other recent data

The anomalies of the curves of Takeda and Turuta (4) seem to be adsorption effects (38). The same is surely true for the curves of Streeter and Boyer (5) and Umstätter (6). Boyer and Streeter expressed the opinion that the adsorption can explain neither the molecular weight dependence of the minimum of the curve nor the time dependence of the viscosity they found (39). But the present author (12) and also Takeda and Endo (38) have later shown that the molecular weight dependence is really to be expected. With reference to the time effect, it seems as though the time dependence of the viscosity is only one factor which effects the efflux time, and thus the apparent viscosity when the solution is stored in contact with the capillary. Umstätter declares in a recent paper (40) that he has convincing evidence, both experimental and theoretical, that the anomalies of viscosity are not caused by an adsorption effect. But since a treatment of this evidence, which is directly related to Umstätter's paper (41), has been published by the present author the latter will not be discussed here. (See also a paper by Boyer (42), especially the discussion.)

With reference to Batzer (19) who states that only branched but not linear molecules give a minimum-maximum in the viscosity curve, the present author has earlier (12) suggested the following explanation. An adsorbed monomolecular layer of spherical molecules probably has a greater thickness than a corresponding layer of linear molecules if we have about the same molecular weight for both types of molecules. Some experiments have been made with the suspended level viscometer (some of the earlier experiments were made with the double viscometer described in reference (11)) to see if this explanation is valid, but as yet no definite answer can be given. But some interesting observations were made in connection with these experiments and will be described here. Two different types of polymers have been investigated: (1) Polymethyl methacrylate, linear, and a branched copolymer of methyl methacrylate and glycol dimethacrylate. These polymers were prepared in collaboration with Dr. A. F. V. Eriksson at this Institute. (2) Polyvinyl acetate, linear and branched. These samples were, as already mentioned, kindly placed at our disposal by Dr. Peaker. The properties of the polymers are given in Table 6.

The measurements with polymethyl methacrylate and the corresponding copolymer seemed at first to verify Batzer's results very well. But then we became suspicious that the copolymer might contain traces of crosslinked polymer gel particles. After 30 minutes of centrifuging in a Spinco model centrifuge at 25,000 r.p.m. the marked difference between the two polymers also disappeared. That only extremely small quantities of gels were necessary to cause this effect is clear from the fact that no visible depositions were to be found in the tubes after the centrifuging, and there were no other signs that the solutions were not true ones. The dissipation of the marked difference between the two fractions does not mean that the above hypothesis about these phenomena is wrong. A copolymer of this kind can only have a few branches per molecule which was also confirmed by sedimentation measurements.

The polyvinyl acetates prepared by Peaker seemed to us to be suitable for an investigation of this type. It is true that Peaker had observed signs that the branched polymers with the highest branching frequency were not totally soluble, but this was not the case for the fraction we received. From our work with the branched polymer

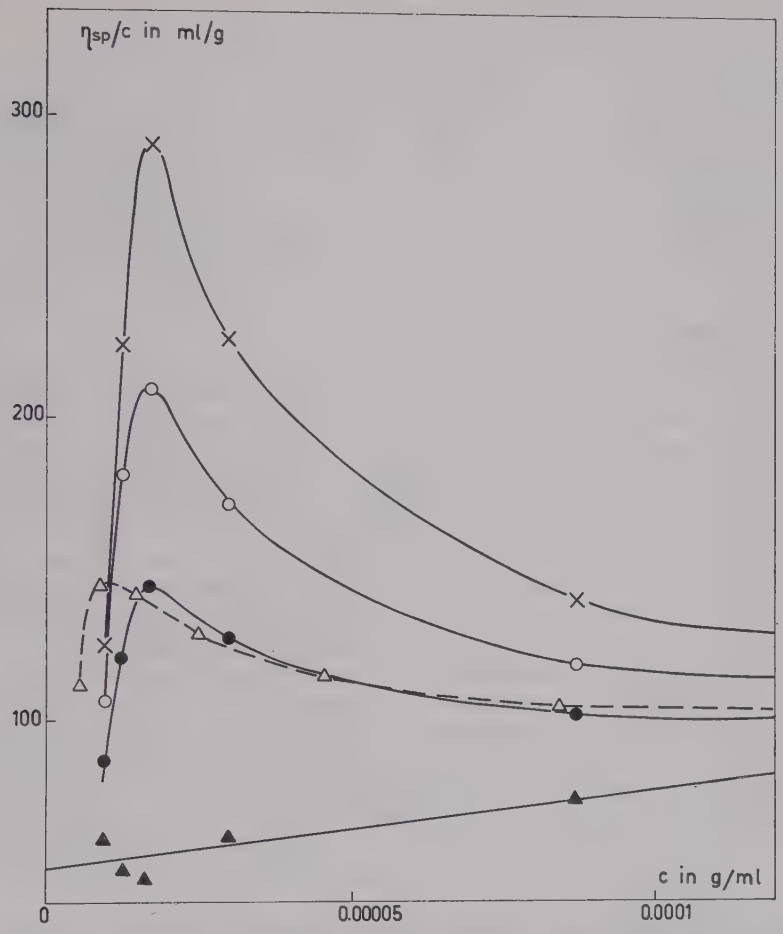

Fig. 17. Viscosity curves for branched polyvinyl acetate. True $\eta_{sp}/c = f(c)$, ▲. Uncorrected $\eta_{sp}/c = f(c)$: ●, for $d = 0.5$ mm; ○, for $d = 0.3$ mm: ×, for $d = 0.2$ mm. (----, linear polyvinyl acetate; obtained with the S3 viscometer; $d = 0.2$ mm.)

we think, however, that it is clear from various observations that also here a cross-linking unfortunately had occurred. Nevertheless we used it for some measurements. Before these were undertaken, we first centrifuged the stock solution at about 3000 r.p.m. (rotor radius ~10 cm) for 30 minutes, and then we filtered it twice through G4 filters. Figure 17 gives the viscosity curves for this branched fraction. The dotted line is the corresponding curve of the linear fraction obtained with the S3 viscometer, i.e. the same curve as the highest one in Fig. 7. There is a much more accentuated maximum for the branched fraction than for the linear one. But it is of course doubtful if this effect is due to branched molecules or gel particles. The thickness of the adsorbed layer is greater than that of the linear fraction, this is true, but it is not unreasonably great. With a value of 1200 Å at the concentration 0.0001 g/ml it is still much smaller than that given by Tuijnman and Hermans

(~5000 Å) (8). While centrifuging the solution in a Spinco centrifuge at 25,000 r.p.m. for 30 minutes, there were possibly some very weak traces of gels.

All this shows very distinctly, however, that we must proceed with the greatest caution when working with branched molecules prepared according to methods where cross-linking is not totally avoided. For instance it seems very probable that the different peculiar viscosity effects obtained by Peaker with that branched polymer may be explained by the presence of gel particles. (See also next paragraph.)

In several other papers it is stated that the viscosity anomalies of the type minimum and eventual maximum in the η_{sp}/c vs. c curve cannot be explained as an adsorption effect. Kapadia for instance asserts this opinion. He found anomalies of this type for some different rubber solutions (43). Later he stated (44), that direct adsorption experiments with glass wool showed that practically no adsorption took place. The constancy of the concentration was determined viscometrically. He also reported that some preliminary observations indicated that an uncoiling effect in the dilution caused the anomalies obtained. Unfortunately very few details have been given, and for this reason it is unprofitable to discuss this work. The same may be said about a short summary by Kapur and Gundiah (45), where the high viscosity at low concentrations is stated to "be attributed to the extension and disentangling of polymer chains". Nevertheless some general comments may perhaps be permitted. Kapadia mentions (reference (43), p. 196) that two of the solutions of rubber were not easily filtered through a No. 4 sintered glass disc. This may of course indicate that gel particles were present, and it has already been pointed out that those cause very marked maxima in the viscosity curve. It may also be mentioned here in connection to the uncoiling hypothesis that Batzer's results with branched and linear polymers seem to be inconsistent with the same. An uncoiling hypothesis ought to demand that the linear molecules are more sensitive to dilution than the branched ones. Experiments with linear and branched polyelectrolytes would give a corresponding, amplified difference. Any really suitable measurements for such a comparison do not seem to have been made, but the work of Schaefgen and Trivisonno (46) with linear and multichain polyamides of the same chemical composition may indicate that for polyelectrolytes the uncoiling of linear molecules affects the viscosity more than that of branched molecules.

Very recently a paper has been published by Hirai (47), where he examines thoroughly most of the papers on viscometric anomalies and explains theoretically such anomalies as pure viscosity effects. But for the theoretical interpretation he assumes that the concentration of the minimum is a "critical" one and, as it has now been shown that this assumption is incorrect, this evidence probably does not have any value.

Kawai and Saito (36) on the other hand modified Huggins' equation by means of an expression, Eq. (11), for the concentration dependence of the expansion factor α. In that way they deduce an equation that at least qualitatively describes the minimum of the viscosity curves obtained. The dependence of the shape of the curve and of the position of the minimum on the molecular weight is quite adequate. An examination of their course of action shows that they first give evidence that k' in Huggins' equation

$$\eta_{sp}/c = [\eta] + k'[\eta]^2 c \tag{14}$$

is not a real constant. Then they deduce a new expression for k' but also substitute for the constant term $[\eta]$ an expression due to Flory

$$[\eta] = K M^{\frac{1}{2}} \alpha^3. \qquad (15)$$

Finally they substitute α with an expression in which the concentration dependence of α is included. *They cannot state the reason for this change of the constant term* $[\eta]$. This is important since it is the expansion of this term that actually causes the "bending up" of their theoretical curve. The contribution of the other term to η_{sp}/c is only a few per cent in the interval of low concentrations, and in addition this term decreases with decreasing concentration. Further it may be mentioned that unreasonable high values of α are demanded to explain the increase of η_{sp}/c by several hundred per cent, which sometimes has been obtained in certain experiments.

SUMMARY

The purpose of this work has been to study the viscometric behaviour of extremely dilute solutions of high polymers. Especially the concentration interval around the so-called "critical concentration" has been examined in detail.

1. Equipment for the very precise determination of viscosity is described. Details of special interest are:

(*a*) Ostwald viscometer; totally enclosed during measurements; the liquid comes to the upper viscometer bulb when the whole viscometer is tilted; the volume of working liquid redetermined at each run; special arrangements to avoid errors due to drainage.

(*b*) Suspended level viscometer; three different viscometers in one with different diameters of capillary to be able to correct for the adsorption error under No. 2*a* below; totally enclosed during measurements; the liquid comes to the upper viscometer bulbs when the whole viscometer is tilted.

(*c*) Thermostat with proportional control of temperature.

(*d*) Photographic method to measure efflux time.

2. In the discussion of error especially two errors have been treated:

(*a*) Adsorption error due to the fact that adsorption diminishes the diameter of the capillary.

(*b*) Kinetic energy error. A modified method for the determination of the kinetic energy correction has been submitted.

3. Curves of η_{sp}/c vs. c have been obtained using different capillary diameters and clearly show that *the usual anomalies of viscosity curves at very low concentrations are only due to adsorption effects.*

4. Curves of η_{sp}/c vs. c corrected for adsorption effects are perfectly linear down through the "critical concentration" interval.

5. Certain indications have been observed that there is a "bending down" of the viscosity curve at concentrations *much lower* than the calculated "critical concentration".

6. It has been shown that the great gradient dependence, pointed out by Tuijnman and Hermans, does not occur.

7. Effects similar to those of Batzer with branched and linear polymers have been obtained. These effects are due to adsorption, but it could not be decided definitely whether the adsorption layer of the branched polymer contains traces of gel particles and thus is more accentuated.

8. Some recent theoretical calculations that the usual anomalous viscosity curves in reality are true ones, are shown not to be convincing.

9. Adsorption isotherms giving a (= the thickness of the adsorbed layer) vs. c have been obtained from viscosity values.

10. The curve of a vs. c has a maximum at a rather high concentration. This may be due to a compression of the molecules with increasing concentration. A comparison is given between this curve and a theoretical curve taking account of the concentration dependence of the expansion factor α.

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